

What is claimed is:

1. A method for forming a silicon dioxide film on the surface of a substrate using a catalyst-assisted atomic layer deposition process, said method comprising the sequential steps of:

5 (a) feeding a halogen- or NCO- substituted siloxane as a first reactant onto a substrate to form a chemisorbed layer comprising the first reactant; and

(b) feeding a second reactant onto the chemisorbed layer to form the silicon dioxide film on the substrate.

10 2. The method according to claim 1, wherein the first reactant is a siloxane represented by the formula $\text{Si}_n\text{O}_{n-1}\text{X}_{2n+2}$, where n is an integer of 2 to 5, and X is a chemical group selected from F, Cl, Br, I or NCO.

15 3. The method according to claim 1, wherein the first reactant is a halogen- or NCO- substituted disiloxane.

4. The method according to claim 1, wherein the first reactant is selected from the group consisting of Si_2OCl_6 , Si_2OBr_6 , and $\text{Si}_2\text{O}(\text{NCO})_6$.

20 5. The method according to claim 1, wherein the second reactant is a component selected from the group consisting of oxygen (O) atoms in compound or radical form.

25 6. The method according to claim 5, wherein the second reactant is selected from H_2O , H_2O_2 , ozone (O_3) or oxygen radical.

7. The method according to claim 1, wherein in step (a), the first reactant is fed onto the substrate together with a first basic catalyst.

30 8. The method according to claim 1, wherein in step (b), the second reactant is fed onto the substrate together with a second basic catalyst.

9. The method according to claim 1, wherein steps (a) and (b) are carried out at a temperature of about 25-500°C.

10. The method according to claim 1, wherein steps (a) and (b) are carried out under a pressure of about 0.1-100 Torr.

5 11. The method according to claim 1, wherein in steps (a) and (b), the first and the second reactants are fed onto the substrate together with an inert gas.

12. The method according to claim 1, further comprising the steps of repeating steps (a) and (b) sequentially until a silicon dioxide film having a predetermined thickness greater than two SiO₂ monolayers is thereby formed.

13. The method according to claim 12, further comprising the step of annealing the silicon dioxide film after the final step (b).

15 14. The method according to claim 13, wherein the annealing step is carried out using a process selected from a heat treatment, a plasma treatment, or an ozone treatment.

20 15. The method according to claim 13, wherein the annealing is carried out at a temperature of about 500-900°C under an atmosphere of N₂, O₂, H₂, Ar, or mixtures thereof, a combination of N₂ and O₂ gas, or an NH₃ gas.

25 16. The method according to claim 13, wherein the annealing step is carried out using a plasma treatment at a temperature of about 200-700°C under an atmosphere of an O₂ or H₂ gas.

30 17. The method according to claim 13, wherein the annealing step is carried out using an ozone treatment within a temperature range between room temperature and about 700°C.

18. The method according to claim 1, further comprising first and second byproduct removal steps of removing at least a first byproduct from the region surrounding the substrate after step (a) and removing at least a second byproduct from the region surrounding the substrate after step (b).

19. The method according to claim 18, wherein the first and the second byproduct removal steps are carried out by means of (i) an inert gas purge, (ii) an evacuation under a pressure lower than when the first and the second reactants respectively are fed onto the substrate, or (iii) an inert gas purge and evacuation in combination.

20. The method according to claim 1, further comprising the step of preheating the substrate to a temperature of about 25-500°C before step (a).

21. A method for forming a silicon dioxide film on the surface of a substrate using a catalyst-assisted atomic layer deposition process, said method comprising the sequential steps of:

- (a) loading a substrate in a chamber;
- (b) introducing a siloxane compound represented by the formula $\text{Si}_n\text{O}_{n-1}\text{X}_{2n+2}$, where n is an integer of 2 to 5, and X is a chemical group selected from F, Cl, Br, I or NCO, as a first reactant together with a first catalyst into the chamber to produce a chemisorbed layer comprising the first reactant on the substrate;
- (c) removing at least a byproduct of step (b) from the chamber;
- (d) introducing a second reactant together with a second catalyst into the chamber to react with the chemisorbed layer on the substrate to produce a silicon dioxide film on the substrate; and
- (e) removing at least a byproduct of step (d) from the chamber.

22. The method according to claim 21, further comprising the steps of repeating steps (a) through (e) sequentially until a silicon dioxide film having a predetermined thickness greater than two SiO_2 monolayers is thereby formed.

23. The method according to claim 21, further comprising the step of preheating the substrate to a temperature of about 25-500°C after step (a) and before step (b).

24. The method according to claim 21, wherein the first reactant is selected from the group consisting of Si_2OCl_6 , Si_2OBr_6 and $\text{Si}_2\text{O}(\text{NCO})_6$.

25. The method according to claim 21, wherein the second reactant is a component selected from the group consisting of oxygen (O) atoms in compound or radical form.

26. The method according to claim 25, wherein the second reactant is selected from the group consisting of H_2O , or H_2O_2 , ozone (O_3) and oxygen radical.

27. The method according to claim 21, wherein the first and second catalysts are pyridine or amine, respectively.

28. The method according to claim 21, wherein steps (b) and (d) are carried out at a temperature of about 25-500°C.

29. The method according to claim 21, wherein steps (b) and (d) are carried out under a pressure of about 0.1-100 Torr.

30. The method according to claim 21, wherein, in steps (b) and (d), the first and the second reactants are introduced into the chamber together with an inert gas.

31. The method according to claim 21, wherein steps (c) and (e) are carried out by means of a step selected from: (i) an inert gas purge, (ii) an evacuation under a pressure lower than when the first and the second reactants are introduced into the chamber, and (iii) an inert gas purge and evacuation used in combination.

32. The method according to claim 21, further comprising the step of annealing the silicon dioxide film after step (e).

33. The method according to claim 32, wherein the annealing step is carried out using a heat treatment, a plasma treatment, or an ozone treatment.

34. A method for forming a silicon dioxide film on the surface of a substrate for semiconductor applications using a catalyst-assisted atomic layer deposition process, said method

5 comprising at least the sequential steps of exposing a functionalized surface of the substrate to a first reactant mixture consisting essentially of first reactant and first catalyst and thereafter exposing that surface to a second reactant mixture consisting essentially of second reactant and second catalyst to form a silicon dioxide monolayer on the substrate surface, wherein

10 the first reactant consists essentially of at least one member selected from the group consisting of halogen- or NCO-substituted siloxanes.

35. The method according to claim 34, wherein the first reactant consists essentially of a siloxane represented by the formula $\text{Si}_n\text{O}_{n-1}\text{X}_{2n+2}$, where n is an integer of 2 to 5, and X is a chemical selected from the group consisting of F, Cl, Br, I or NCO.

36. The method according to claim 34, wherein the first reactant is halogen- or NCO-substituted disiloxane.

20 37. The method according to claim 36, wherein the first reactant is selected from the group consisting of Si_2OCl_6 , Si_2OBr_6 , or $\text{Si}_2\text{O}(\text{NCO})_6$.

38. The method according to claim 34, wherein said first catalyst is selected from the group consisting of pyridine and amine.

25 39. The method according to claim 34, wherein said first catalyst consists essentially of a tertiary aliphatic amine compound having the general formula NR_3 , where each R represents the same or a different aliphatic group having from 1 to 5 carbon atoms.

40. The method according to claim 34, wherein said first catalyst consists essentially of trimethyl amine.

41. The method according to claim 34, wherein said first reactant consists essentially of Si_2OCl_6 and said first catalyst consists essentially of trimethyl amine.

42. The method according to claim 34, wherein the steps are carried out at a temperature ranging from about 25-500°C.

43. The method according to claim 34, wherein the steps are carried out at a pressure ranging from about 0.1-100 Torr.

44. The method according to claim 34, wherein the first catalyst and second catalyst are the same.

45. The method according to claim 34, wherein said method further comprises the steps of removing unreacted reactant, the first catalyst, the second catalyst and reaction byproducts from the region of the substrate following each step.

46. The method according to claim 35, wherein said method further comprises the steps of removing unreacted reactant, the first catalyst, the second catalyst and reaction byproducts from the region of the substrate following each step.

47. The method according to claim 45, wherein the first reactant, second reactant, the first catalyst and the second catalyst are each supplied to the substrate surface by separate feed lines.

48. The method according to claim 47, comprising the following deposition cycle: (a) a first reaction period during which first reactant and catalyst are fed through their respective feed lines to the substrate surface along with inert gas fed through the second reactant feed line; (b) a first purge period during which the feeds of first reactant and catalyst are stopped and, instead, inert gas is fed through the first and second reactant and catalyst feed lines; (c) a second reaction period during which second reactant and catalyst are fed through their respective feed lines to the substrate surface along with inert gas fed through the first reactant feed line; and (d) a second purge period during which the feeds of second reactant and catalyst are

stopped and, instead, inert gas is fed through the first and second reactant and catalyst feed lines.

49. The method according to claim 34, further comprising the steps of repeating the deposition cycle multiple times on the same substrate to obtain a silicon dioxide film of a desired thickness.

50. The method according to claim 48, further comprising the steps of repeating the deposition cycle multiple times on the same substrate to obtain a silicon dioxide film of a desired thickness.

51. The method according to claim 34, further comprising a step of annealing the deposited silicon dioxide film

52. The method according to claim 51, wherein the annealing step is selected from one of the following:

a heat treatment at a temperature of about 500-900°C under an atmosphere of N₂, O₂, H₂, Ar, and mixtures thereof, a combination of N₂ and O₂ gas, or an NH₃ gas;

a plasma treatment about 200-700°C under an atmosphere of an O₂ or H₂ gas; or

an ozone treatment within a temperature range between about room temperature and about 700°C.

53. The method according to claim 34, comprising for each atomic layer deposition a purge-pumping procedure according to the following sequence: feeding the first reactant and first catalyst to a region containing the substrate during a process time period t_1 ; purging the region with an inert gas during a time period t_2 immediately following period t_1 ; pumping the region to at least partially evacuate inert gas and other gaseous materials from the region during a time period t_3 immediately following period t_2 ; feeding the second reactant and second catalyst to the region during a time period t_4 immediately following period t_3 ; purging the region with an inert gas during a time period t_5 immediately following period t_4 ; and pumping the

region to at least partially evacuate inert gas and other gaseous materials from the region during a time period t_6 immediately following period t_5 .

54. The method according to claim 34, comprising for each atomic layer deposition a pumping-purge procedure according to the following sequence: feeding the first reactant and first catalyst to a region containing the substrate during a process time period t_1 ; pumping the region to at least partially evacuate gaseous materials from the region during a time period t_2 immediately following period t_1 ; purging the region with an inert gas during a time period t_3 immediately following period t_2 ; feeding the second reactant and second catalyst to the region during a time period t_4 immediately following period t_3 ; pumping the region to at least partially evacuate gaseous materials from the region during a time period t_5 immediately following period t_4 ; and, purging the region with an inert gas during a time period t_6 immediately following period t_5 .

55. A semiconductor device comprising a substrate having a silicon dioxide film of enhanced quality deposited on a surface thereof, wherein said film has been formed by a method according to claim 1.

56. A semiconductor device comprising a substrate having a silicon dioxide film of enhanced quality deposited on a surface thereof, wherein said film has been formed by a method according to claim 21.

57. A semiconductor device comprising a substrate having a silicon dioxide film of enhanced quality deposited on a surface thereof, wherein said film has been formed by a method according to claim 34.